

X-ray photoelectron spectroscopy studies of the early-stage oxidation behavior of (Pt, Ni)₃Al(1 1 1) surfaces in air

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Abstract

We have studied the early-stage of oxide formation on (111)-oriented (Pt,Ni)₃Al single crystals in air. From X-ray photoelectron spectroscopy (XPS), the predominant surface oxide changed from NiO to Al₂O₃, as oxidation temperature increased from 900 to 1300 K. Some NiAl₂O₄ (spinel) also formed at the higher temperatures. Under conditions where NiO and/or NiAl₂O₄ were present, it resided atop a layer of aluminum oxide, mixed in some cases with metallic Ni. By comparing samples that contained 0, 10 and 20 at% Pt in the bulk, we found that the effects of Pt were to (1) promote the preferential formation of aluminum oxide over nickel oxide(s) in the top layer at all temperatures studied, (2) suppress the amount of metallic Ni mixed with Al₂O₃ in the underlying oxide region, (3) reduce the total oxide layer thickness, and (4) sharpen the interface between the oxide and the metallic alloy. Published by Elsevier B.V.

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1. Introduction

Nickel aluminides are used as coatings and structural materials for high-temperature applications owing to their excellent oxidation resistance in air at elevated temperatures [1–3]. Nevertheless, improving the oxidation resistance of nickel aluminide has been a major motivation of high-temperature oxidation research. Recent studies have shown that adding Pt to the nickel aluminide Ni₃Al can significantly improve its oxidation resistance at elevated temperatures by promoting the preferential formation of an adherent, Al₂O₃-rich scale [4,5]. To elucidate this beneficial effect of Pt, knowledge of the early-stage oxidation behavior is needed.

Previous studies reported that the establishment and growth of a continuous Al₂O₃ scale on Ni–Al and Fe–Al alloys proceeds via two stages [6–8]: (1) early-stage, transient oxidation; and (2) steady-state oxidation. The possible oxides formed during the early-stage are NiO, NiAl₂O₄ (spinel) and Al₂O₃, in order of increasing thermodynamic stability [9,10]. Under suitable growth conditions, such as isothermal oxidation of a sufficiently thick alloy, Al₂O₃ eventually becomes the steady-state scale. Following establishment of the Al₂O₃ scale, the rate of further oxidation (steady-state oxidation) is drastically decreased and is determined by the scale's effectiveness as a barrier to transport of reactants [6].

The characteristics of the early-stage oxide are believed to have an important influence on the later steady-state growth. In this work, the early-stage oxidation behavior at temperatures in the range 900–1300 K is investigated. By comparing Ni₃Al samples with and without Pt, we gain insight into the role of Pt in the formation of the protective phase.

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While the present paper deals with early-stage oxidation in air, oxidation at lower pressure can provide insight into the *extreme* initial stage of oxidation. A number of such studies have focused on Ni₃Al [11–15], though only two have dealt with the effect of Pt addition [2,16]. Using this approach, we [2] previously reported that the predominant oxide on (111)-oriented Ni₃Al was NiO, capped by a thin layer of Al oxide at low temperature (<700 K). Above 700 K, the oxide consisted of a thicker, exclusive layer of Al oxide. The effect of Pt was to reduce the amount of both oxides at all temperatures, and to shift the establishment of the thick Al oxide layer to lower temperatures. Similar conclusions will be drawn from the present work, indicating that Pt probably affects oxidation processes similarly at both the start, and the continuation, of the so-called early-stage.

2. Experimental description

Many XPS experimental details have been published elsewhere [2,17]. All spectra were measured at an emission angle of 45°.

Bulk compositions of the single-crystal samples, measured with electron probe microanalysis, were as follows: Pt₀Ni_{77.4±0.3}Al_{22.6±0.3} (called 0%-Pt), Pt_{9.7±0.1}Ni_{65.3±0.3}Al_{25.0±0.3} (called 10%-Pt), and Pt_{20.4±0.1}Ni_{54.7±0.2}Al_{24.9±0.2} (called 20%-Pt). The samples were spatially homogeneous within the quoted uncertainties. Specimens for analysis were (111)-oriented, cut, and then polished down to a final treatment with 1 μm diamond paste in air.

The polished samples were then oxidized in a tube furnace lined with a 19 mm diameter fused silica tube. Ultra-high purity/zero grade air flowed through the tube at 10 cm³/min. The three samples of different Pt content were placed at the same time on a platinum tray mounted on a 1.6 mm diameter type K thermocouple (TC) probe for sample temperature monitoring. The furnace was preheated to a temperature 20 K above the oxidation temperature, and then allowed to stabilize. The samples were inserted into the furnace on the TC probe-tray and the exposure time was measured from the time this probe reached the set temperature. The probe-tray was withdrawn from the furnace after the desired exposure time and was permitted to air cool. Fig. 1 shows a typical temperature vs. time profile of a sample during heating and cooling cycles. As shown in Fig. 1, it took approximately 60 s for the sample to reach 900 K. In addition to the three samples, a NiO standard was produced by heating a pure Ni foil in ultrahigh purity/zero grade air at 1100 K for 4 h.

The spot analyzed in XPS was a rectangle, 0.8 mm × 2 mm in size. SEM of the oxidized surfaces revealed the oxide to be spatially homogeneous on this length scale.

Exposure to air in our experiments left not only surface oxide, but also carbon contamination. As a result, the displacement of the binding energy (BE) of the contaminant C(1s) peak from a standard value of 285.0 eV could be used to calibrate the energy scale in XPS.

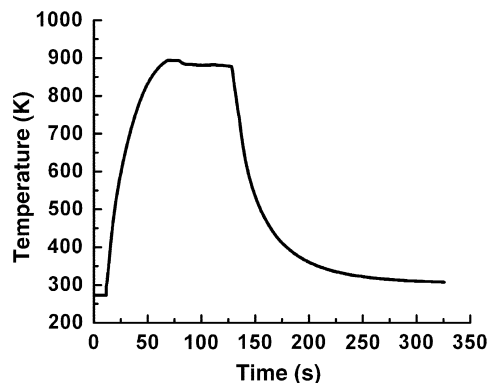


Fig. 1. A sample surface temperature profile during heating and cooling cycles. In this case, it took approximately 60 s for the sample to reach 900 K. Times reported in this paper describe the time spent at temperature, not including heating and cooling.

XPS depth profiles were obtained by ion etching the surface with a 4 keV Ar⁺ rastered ion beam at normal incidence. The correlation between etching time and analyzed depth was calibrated separately using SiO₂ films of known thickness. The sputtering rate was ~3 nm/min. Depth profiles are reported in terms of atomic concentrations of individual elements vs. time. To obtain the atomic concentrations, elemental sensitivity factors appropriate to the analyzer (PHI 5500) were used to estimate chemical composition from integrated intensities of core level transitions [18]. The Shirley background subtraction method [19] was applied in this study. However, the atomic concentrations were quite sensitive to the endpoints selected to define the peak areas, so they were used more as a measure of relative values (e.g., comparing data at different temperatures or different Pt concentrations) rather than a measure of absolute values (e.g., determining the stoichiometry of an oxide).

3. Experimental results and interpretation

3.1. XPS peak assignments

XPS is the basis for determining whether an element exists as the metal or as the oxide, and for distinguishing different types of oxide. To aid in that determination, Table 1 summarizes binding energies (BEs) and some other spectral characteristics, both from the literature and from the present work, for the metal lines of the major species that will be considered [15,18,20–30]. In the XPS data, overlap between lines of Pt, Ni, and Al prevented use of certain peaks that are considered standards. In particular, the Al2p could not be used because it overlapped completely with the Pt4f_{5/2}, and both were close to the Ni3p. These issues led us to choose the Al2s, Ni2p_{3/2}, and Pt4d_{5/2} from among the metal peaks for analysis.

In addition to the metal lines, the O1s line can be useful; however, it can contain contributions from a myriad of possible species after air oxidation. Also, a survey of the literature suggests that the value reported for the O1s BE of a

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